

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 488 235 B1**

(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention  
of the grant of the patent:  
18.09.1996 Bulletin 1996/38

(51) Int. Cl.<sup>6</sup>: **B01D 53/02**, C10G 25/00,  
C07C 7/12, C10G 70/04

(21) Application number: 91120301.6

(22) Date of filing: 27.11.1991

### (54) Sorption of trialkyl arsines

Sorption von Trialkylarsinen

Sorption des trialkyl arsines

(84) Designated Contracting States:  
BE DE ES FR GB IT NL

(30) Priority: 28.11.1990 US 619166

(43) Date of publication of application:  
03.06.1992 Bulletin 1992/23

(73) Proprietor: PHILLIPS PETROLEUM COMPANY  
Bartlesville Oklahoma 74004 (US)

(72) Inventors:  
• Nowack, Gerhard Paul  
Bartlesville, OK 74006 (US)

• Cheung, Tin-Tack Peter  
Bartlesville, OK 74006 (US)

(74) Representative: Dost, Wolfgang, Dr.rer.nat., Dipl.-  
Chem. et al  
Patent- und Rechtsanwälte  
Bardehle . Pagenberg . Dost . Altenburg .  
Frohwitter . Gelssler & Partner  
Postfach 86 06 20  
81633 München (DE)

(56) References cited:  
EP-A- 0 107 582 WO-A-90/10684  
US-A- 4 933 159 US-A- 5 024 683

**EP 0 488 235 B1**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

## Description

### Background of the Invention

5 This invention relates to the removal of trialkyl arsines from fluids by means of solid sorbents. In another aspect, this invention relates to the removal of trialkyl arsines from gases, in particular hydrocarbon-containing gases.

A material for removing of elemental metal such as Hg and As is known from WO-A-90/10684. However, this material is not very effective for the removal of metal compounds such as arsines comprising hydrocarbon chains of 2 and more C atoms.

10 Also, WO-A-30/10684 describes a process for elimination of mercury in hydrocarbon charges wherein said charge is contacted, under hydrogen, with a catalyst containing at least one metal from the group consisting of nickel, cobalt, iron and palladium followed by - or mixed with - a capture mass containing sulfur or a metal sulfide.

Materials for adsorbing and/or absorbing unsubstituted arsine ( $\text{AsH}_3$ ) are well known as well. However, many of these materials are ineffective for the sorption of trialkyl arsines, which may be present as undesirable impurities in natural gas streams produced at some well sites. The present invention provides a sorbent material which is effective for removing trialkyl arsines from fluids by sorption (i.e. adsorption and/or absorption).

### Summary of the Invention

20 It is an object of this invention to provide a process for removing trialkyl arsines from fluids. It is another object of this invention to provide a process for removing trialkyl arsines from gases, in particular hydrocarbon-containing gases. Other objects will become apparent from the detailed description of the invention and the appended claims.

In accordance with this invention, a process for at least partially removing trialkyl arsines from fluids (preferably gases) comprises the step of contacting a fluid feed which contains at least one trialkyl arsine with a solid sorbent material exclusively consisting of (a) elemental sulfur and (b) an inorganic support material (preferably selected from alumina, fluorided alumina, aluminum phosphate, magnesia, silica, aluminosilicates (such as clays and zeolites), titania, zirconia, hafnia, zinc oxide, zinc aluminate, aluminates of metals of Group IIA of the Periodic Table [as defined on page 852 of Webster's New Collegiate Dictionary, 1977], zinc titanate, titanates of Group IIA metals, activated carbon, and mixtures of the above materials); wherein said contacting is carried out at such contacting conditions as to obtain a fluid product having a lower trialkyl arsine content than said feed (with the spent sorbent material containing the portion of trialkyl arsine which has been removed from the feed). Moreover, contacting the fluid with the sorbent material is not preceded by contacting the fluid with a catalyst.

### Detailed Description of the Invention

35 The term "trialkyl arsine", as used herein, refers to compounds having the general chemical formula of  $\text{R}_3\text{As}$ , wherein each R is a radical independently selected from among alkyl groups (straight and/or branched), preferably having 1-6 (more preferably 1-3) carbon atoms. Particularly preferred trialkyl arsines are trimethyl arsine, triethyl arsine, dimethyl ethyl arsine and diethyl methyl arsine.

40 Any suitable liquid or gaseous fluid stream which contains trialkyl arsine(s) can be used as feed in the process of this invention. Preferably, the feed is gaseous. Non-limiting examples of suitable feeds are: natural gas; gaseous petroleum fractions comprising paraffins and olefins containing 1-6 carbon atoms per molecule; and gaseous products from thermal and catalytic cracking of petroleum, shale oil or coal. Generally, the gases comprise methane, ethane, ethylene, propane, propylene, n-butane, isobutane, butenes; and the like. These gas streams can contain other impurities, such as hydrogen sulfide, carbonyl sulfide (COS), mercaptans, organic sulfides, mercury and/or compounds thereof, carbon monoxide, carbon dioxide, inert gases ( $\text{N}_2$ , He, Ne, Ar), and the like.

45 Other arsenic compounds may also be present in the fluid stream which is treated by the process of this invention, such as  $\text{AsH}_3$ ,  $\text{RAsH}_2$ ,  $\text{R}_2\text{AsH}$ , and the like, wherein R is an alkyl group, as defined above. It is also possible to have triphenyl arsine; dialkyl phenyl arsines, dialkyl cycloalkyl arsines, and the like present in the feed. Preferably, free oxygen is substantially absent from the feed.

Generally, the total concentration of the trialkyl arsine(s) in the feed (preferably gaseous) is in the range of from about 1 ppb As (1 part by weight of arsenic per billion parts by weight of feed) to about 0.1 weight-% As, preferably about 0.01-10 ppm As (parts by weight of arsenic per million parts by weight of feed). The concentrations of the other impurities and the exact composition of the feed will widely vary from feedstock to feedstock.

50 The sorbent materials which are used in the process of this invention comprise elemental sulfur and an inorganic support material. Generally the sulfur content in the sorbent is in the range of from about 1 to about 50, preferably from about 3 to about 25, weight-% elemental S.

Any suitable, effective inorganic support material can be employed as component (b). Preferably, the support material is selected from the group consisting of alumina, fluorided alumina (i.e., alumina which has been treated with HF or

$\text{NH}_4\text{HF}_2$  under such conditions as to incorporate fluoride ions into the crystal lattice of alumina), aluminum phosphate, magnesia ( $\text{MgO}$ ), silica, titania ( $\text{TiO}_2$ ), zirconia ( $\text{ZrO}_2$ ), hafnia ( $\text{HfO}_2$ ), zinc oxide, zinc aluminate ( $\text{ZnAl}_2\text{O}_4$ ) aluminates of Group IIA metals (i.e., of Be, Mg, Ca, Sr, Ba), zinc titanate ( $\text{Zn}_2\text{TiO}_4$ ), titanates of Group IIA metals, activated carbon, and mixtures of two or more than two of the above materials. Presently more preferred support materials are alumina, silica, titania, activated carbon, and mixtures of two or more of these materials.

The elemental sulfur component (a) can be combined with the inorganic support material (b) in any suitable manner, such as by impregnating or spraying the support material with a solution of sulfur (e.g., in carbon disulfide or another effective solvent for sulfur), followed by drying of the sulfur-containing material; or by impregnating the support material with molten sulfur; or by subliming sulfur onto the support material.

The sorbent particles of this invention can have any suitable surface area (preferably about 10-1000  $\text{m}^2/\text{g}$ , as measured by the B.E.T. method employing  $\text{N}_2$ ), any suitable shape (such as spherical, cylindrical, ring-shaped, trilobal etc.), and any suitable size (such as about 0.2-20 mm diameter for spherical particles).

Any suitable contacting conditions can be employed in the sorption process of this invention. Generally, the temperature in the contacting zone is in the range of from about  $-20$  to about  $100^\circ\text{C}$ , preferably about  $20$  to about  $50^\circ\text{C}$ . Generally, the pressure in the contacting zone is in the range of from about 100 kPa to about 50 MPa (about 1 to about 500 atm.), preferably about 100 kPa to about 7 MPa (about 1 to about 70 atm.). Generally, the gas hourly space velocity of the gaseous feed in the contacting zone is in the range of from about 10 to about 20,000 volume of feed/volume of sorbent/hour, preferably about 1,000 to about 10,000 volume/volume/hour, measured at about  $25^\circ\text{C}/0.1$  MPa (about  $25^\circ\text{C}/1$  atm.). Generally, the contacting is continued until trialkyl arsine breakthrough occurs, i.e., when the treated product contains more trialkyl arsines than can be tolerated, such as about 50 ppb.

Treatment of the feed streams in accordance with the process of this invention can be carried out in any suitable manner. For example, in a preferred embodiment a bed of the sorbent is placed as a fixed bed in a confined zone, and a fluid stream (preferably a gas) is passed therethrough in either upward or downward flow. Other suitable, yet less preferred methods of treatment can include a fluidized operation in which the feed and the sorbent particles are maintained in a state of turbulence under hindered settling conditions in a confined zone, moving bed operations in which the sorbent passes as a moving bed countercurrently to or concurrently with the feed, etc. In a fixed bed operation of a continuous process, the flow of fluid can be rotated between two or more sorbent beds with at least one being in regular operation, the other being in a regeneration mode. Continuous processes are preferred, but it is understood that batch type operations can be employed when desired.

It is within the scope of this invention to employ a combination of sorbents, such as a first bed (guard bed) of a supported  $\text{CuO-ZnO}$  material (described in U.S. Patent 4,593,148) or  $\text{PbO/Al}_2\text{O}_3$  for substantial removal of  $\text{AsH}_3$  and/or  $\text{H}_2\text{S}$  from the feed, and at least one subsequent downstream bed containing the sorbent material of this invention for absorbing trialkyl arsines. This multi-bed operation can be carried out in one reactor containing a layer of the supported  $\text{CuO-ZnO}$  material or  $\text{PbO/Al}_2\text{O}_3$  (or any other known sorbent for  $\text{AsH}_3$  and  $\text{H}_2\text{S}$ ) and a downstream layer of a trialkyl arsine sorbent of this invention. Or the multi-bed operation can be carried out using two (or more) separate sorption reactors: a first reactor containing the supported  $\text{CuO-ZnO}$  material or  $\text{PbO/Al}_2\text{O}_3$  (or any other known sorbent for  $\text{AsH}_3$  and  $\text{H}_2\text{S}$ ) and a second reactor containing the trialkyl arsine sorbent of this invention, wherein the feed passes through the first reactor and thereafter through the second reactor.

The process of this invention will be further illustrated by the following non-limiting examples.

#### Example I

This example illustrates the experimental setup for investigating the absorption of trimethyl arsine by sorbent materials.

A nitrogen gas stream was passed through a flask containing liquid trimethyl arsine (provided by Strem Chemicals, Inc.), which was cooled to about  $-78^\circ\text{C}$  by placing the flask in a dry ice/acetone mixture. The gas stream, which contained  $\text{N}_2$  and trimethyl arsine, was passed through a glass tube of about 7 mm diameter and about 12 cm length containing about 5 grams of one of the sorbents described below. The gas which exited from the absorption tube was passed through an aqueous solution of  $\text{KMnO}_4$  and then to a flow meter. The flow rate of the gas was about 1800  $\text{cm}^3/\text{hour}$  (equivalent to about 360  $\text{cm}^3/\text{cm}^3$  sorbent/hour).

When trimethyl arsine breakthrough occurred (i.e., when the sorbent had reached its maximum arsine absorption capacity), the purple color of the  $\text{KMnO}_4$  solution turned brownish. After arsine breakthrough had been detected, the flow of the trimethyl arsine containing gas stream was stopped, and a purge stream of pure nitrogen was passed through the sorbent material for about 15 hours so as to purge unabsorbed trimethyl arsine therefrom. The absorption tube containing the sorbent and absorbed trimethyl arsine was weighed. The difference between this weight and the initial weight of the tube with fresh sorbent was the weight of absorbed trimethyl arsine.

Example II

This example illustrates the preparation of several absorbents and their capacity for trimethyl arsine sorption.

Sorbent A was sulfur-impregnated alumina containing about 3.3 weight-% S. A 20-40 mesh sample of 1.11 grams of Harshaw Al-3996R alumina (provided by Engelhard Corporation, Edison, NJ) was impregnated with a solution of 0.038 grams of elemental sulfur dissolved in about 1 cm<sup>3</sup> carbon disulfide (CS<sub>2</sub>). The obtained yellow-colored material was partially dried at room temperature. This partially dried material was placed into a tube, and a stream of N<sub>2</sub> was passed through the material.

Sorbent B was a sulfur-impregnated alumina sorbent material which contained 4.8 weight-% S. A sample of 5 grams of 20-40 mesh Alcoa S-201 alumina (provided by Aluminum Company of America, Pittsburgh, PA) was impregnated with a solution of 0.25 grams sublimed sulfur in about 8 cc CS<sub>2</sub>, followed by drying and purging with N<sub>2</sub> (as described for Sorbent A).

Sorbent C was sulfur-impregnated silica containing 4.8 weight-% S. A sample of 3.8 grams of dried, 20-40 mesh silica (Davison Grade 59 silica, provided by Davison Chemical Division of W. R. Grace and Company, Baltimore, MD) was impregnated with a solution of 0.19 grams of sublimed sulfur in CS<sub>2</sub>. The thus-impregnated material was dried and purged with N<sub>2</sub>, substantially in accordance with the procedure for Sorbent A.

Sorbent D was sulfur-impregnated titania containing 3.4 weight-% S. A sample of 4.6 grams of 20-40 mesh titania (Calsicat 47D-26A titania, provided by Mallinckrodt, Inc., St. Louis, MO) was impregnated with a solution of 0.16 grams of elemental sulfur in CS<sub>2</sub>. The thus-impregnated material was dried and purged with N<sub>2</sub>, substantially in accordance with the procedure for Sorbent A.

Sorbent E was sulfur-impregnated activated carbon containing 5 weight-% S. A sample of 2.83 grams of 20-40 mesh dried charcoal, which had been heated at 150°C overnight, was impregnated with a solution of 0.15 grams of sublimed sulfur in CS<sub>2</sub>. The thus-impregnated material was dried and purged with N<sub>2</sub>, substantially in accordance with the procedure for Sorbent A.

Trimethyl arsine tests were carried out with Sorbents A-F in accordance with the procedure described in Example I. Test results, summarized in the Table below, demonstrate that the supported sulfur materials are quite effective as trialkyl arsine sorbents. Additional tests (not described in detail herein) indicated that unimpregnated Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and TiO<sub>2</sub> did not absorb any trimethyl arsine.

Table

Sorbent	Run Time	Absorbed As (Wt.-%)
A (S/Al <sub>2</sub> O <sub>3</sub> )	until As breakthrough	4.4
B (S/Al <sub>2</sub> O <sub>3</sub> )	several hours <sup>1</sup>	1.7
C (S/SiO <sub>2</sub> )	several hours <sup>1</sup>	2.6
D (S/TiO <sub>2</sub> )	several hours <sup>1</sup>	0.9
E (S/activ. C)	several hours <sup>1</sup>	6.3

<sup>1</sup> trimethyl arsine breakthrough had not yet occurred.

Example III

Sulfur-containing alumina sorbent material which was substantially the same as Sorbent A was field-tested at a commercial natural gas compressor station near Roswell, NM. The natural gas contained about 0.5 ppm As, primarily as trimethyl arsine. The stainless steel absorption tubes used in these field tests had a diameter of 1.25 cm (0.5 inch), were 90 cm (3 feet) long, and contained about 70 cm<sup>3</sup> (about 71 g) of the sorbent material. Treatment of the natural gas with the sorbent material removed in excess of 99% of the trimethyl arsine present in the gas.

Claims

1. A process for at least partially removing trialkyl arsines from a fluid characterized by contacting said fluid with a solid sorbent material exclusively consisting of (a) elemental sulfur and (b) an inorganic support material without contacting said fluid with a catalyst prior to contacting the fluid with the sorbent material.

2. The process of claim 1, wherein said fluid is a gas.
3. The process of claim 2, wherein said gas is a hydrocarbon-containing gas.
- 5 4. The process of any of the preceding claims, wherein said trialkyl arsine has the formula  $R_3As$  with each R being independently selected from alkyl groups containing 1 - 6 carbon atoms.
5. The process of claim 4, wherein said alkyl groups contain 1 - 3 carbon atoms.
- 10 6. The process of any of claims 2 - 5, wherein said trialkyl arsine is selected from trimethyl arsine, triethyl arsine, dimethyl ethyl arsine and diethyl methyl arsine.
7. The process of any of the preceding claims, wherein said fluid contains from 1 ppb to 0.1 weight-% arsenic.
- 15 8. The process of any of claims 2 - 7, wherein said fluid contains from 0.01-10 ppm arsenic.
9. The process of any of the preceding claims, wherein said sorbent material contains from 1-50 weight-% elemental sulfur.
- 20 10. The process of claim 9, wherein said sorbent material contains from 3-25 weight-% elemental sulfur.
11. The process of any of the preceding claims, wherein component (b) of said sorbent material is selected from alumina, fluorided alumina, aluminum phosphate, silica, aluminosilicates, magnesia, titania, zirconia, hafnia, zinc oxide, zinc aluminate, aluminates of metals of Group IIA of the Periodic Table, zinc titanate, titanates of Group IIA metals, activated carbon, and mixtures thereof.
- 25 12. The process of claim 11, wherein component (b) of said sorbent material is selected from alumina, silica, titania, activated carbon and mixtures thereof.
- 30 13. The process of claim 12, wherein said sorbent material contains from 2-20 weight-% elemental sulfur.
14. The process of claim 1, wherein said fluid is a gas which additionally contains at least one of  $AsH_3$  and  $H_2S$ .

#### Patentansprüche

- 35 1. Verfahren zur mindestens partiellen Entfernung von Trialkylarsinen aus einem Fluid, gekennzeichnet durch Kontaktieren des Fluids mit einem festen Sorptionsmaterial, das ausschließlich aus (a) elementarem Schwefel und (b) einem anorganischen Trägermaterial besteht, ohne daß das Fluid vor dem Kontaktieren mit dem Sorptionsmaterial mit einem Katalysator in Kontakt gebracht wird.
- 40 2. Verfahren nach Anspruch 1, wobei es sich bei dem Fluid um ein Gas handelt.
3. Verfahren nach Anspruch 2, wobei es sich bei dem Gas um ein kohlenwasserstoffhaltiges Gas handelt.
- 45 4. Verfahren nach einem der vorstehenden Ansprüche, wobei das Trialkylarsin die Formel  $R_3As$  aufweist, wobei die einzelnen Reste R unabhängig voneinander unter Alkylgruppen mit 1-6 Kohlenstoffatomen ausgewählt sind.
5. Verfahren nach Anspruch 4, wobei die Alkylgruppen 1-3 Kohlenstoffatome aufweisen.
- 50 6. Verfahren nach einem der Ansprüche 2-5, wobei das Trialkylarsin unter Trimethylarsin, Triethylarsin, Dimethylethylarsin und Diethylmethylarsin ausgewählt ist.
7. Verfahren nach einem der vorstehenden Ansprüche, wobei das Fluid 1 ppb bis 0,1 Gew.-% Arsen enthält.
- 55 8. Verfahren nach Anspruch 2-7, wobei das Fluid 0,01 bis 10 ppm Arsen enthält.
9. Verfahren nach einem der vorstehenden Ansprüche, wobei das Sorptionsmaterial 1-50 Gew.-% elementaren Schwefel enthält.

10. Verfahren nach Anspruch 9, wobei das Sorptionsmaterial 3-25 Gew.-% elementaren Schwefel enthält.

11. Verfahren nach einem der vorstehenden Ansprüche, wobei die Komponente (b) des Sorptionsmaterials aus der Gruppe Aluminiumoxid, fluoridiertes Aluminiumoxid, Aluminiumphosphat, Siliciumdioxid, Aluminosilicate, Magnesiumoxid, Titanoxid, Zirkoniumoxid, Hafniumoxid, Zinkoxid, Zinkaluminat, Aluminate von Metallen der Gruppe IIA des Periodensystems, Zinktitanat, Titanate von Metallen der Gruppe IIA, Aktivkohle und Gemische davon ausgewählt ist.

12. Verfahren nach Anspruch 11, wobei die Komponente (b) des Sorptionsmaterials aus der Gruppe Aluminiumoxid, Siliciumdioxid, Titanoxid, Aktivkohle und Gemische davon ausgewählt ist.

13. Verfahren nach Anspruch 12, wobei das Sorptionsmaterial 2-20 Gew.-% elementaren Schwefel enthält.

14. Verfahren nach Anspruch 1, wobei es sich bei dem Fluid um ein Gas handelt, das zusätzlich mindestens einen der Bestandteile  $\text{AsH}_3$  und  $\text{H}_2\text{S}$  enthält.

#### Revendications

1. Un procédé pour éliminer au moins partiellement des trialkyl-arsines à partir d'un fluide, caractérisé en ce qu'il consiste à mettre en contact ledit fluide avec un sorbant solide se composant exclusivement (a) de soufre élémentaire et (b) d'un matériau de support non organique sans mettre en contact ledit fluide avec un catalyseur avant la mise en contact du fluide avec le sorbant.

2. Le procédé selon la revendication 1, dans lequel ledit fluide est un gaz.

3. Le procédé selon la revendication 2, dans lequel ledit gaz est un gaz contenant un hydrocarbure.

4. Le procédé selon l'une quelconque des revendications précédentes, dans lequel ladite trialkyl-arsine répond à la formule  $\text{R}_3\text{As}$ , chaque R étant choisi indépendamment parmi les groupes alkyle renfermant de 1 à 6 atomes de carbone.

5. Le procédé selon la revendication 4, dans lequel lesdits groupes alkyle renferment de 1 à 3 atomes de carbone.

6. Le procédé selon l'une quelconque des revendications 2 à 5, dans lequel ladite trialkyl-arsine est choisie parmi la triméthyl-arsine, la triéthyl-arsine, la diméthyl-éthyl-arsine et la diéthyl-méthyl-arsine.

7. Le procédé selon l'une quelconque des revendications précédentes, dans lequel ledit fluide renferme de 1 ppb à 0,1 % en poids d'arsenic.

8. Le procédé selon l'une quelconque des revendications 2 à 7, dans lequel ledit fluide renferme de 0,01 à 10 ppm d'arsenic.

9. Le procédé selon l'une quelconque des revendications précédentes, dans lequel ledit sorbant renferme de 1 à 50 % en poids de soufre élémentaire.

10. Le procédé selon la revendication 9, dans lequel ledit sorbant renferme de 3 à 25 % en poids de soufre élémentaire.

11. Le procédé selon l'une quelconque des revendications précédentes, dans lequel le composant (b) dudit sorbant est choisi parmi l'alumine, l'alumine fluorée, le phosphate d'aluminium, la silice, les aluminosilicates, l'oxyde de magnésium, l'oxyde de titane, l'oxyde de zirconium, l'oxyde d'hafnium, l'oxyde de zinc, l'aluminate de zinc, les aluminates des métaux du groupe IIA du Tableau Périodique, le titanate de zinc, les titanates des métaux du groupe IIA, le carbone activé et leurs mélanges.

12. Le procédé selon la revendication 11, dans lequel le composant (b) dudit sorbant est choisi parmi l'alumine, la silice, l'oxyde de titane, le carbone activé et leurs mélanges.

13. Le procédé selon la revendication 12, dans lequel ledit sorbant renferme de 2 à 20 % en poids de soufre élémentaire.

14. Le procédé selon la revendication 1, dans lequel ledit fluide est un gaz qui contient supplémentaiement au moins un composant de  $\text{AsH}_3$  et  $\text{H}_2\text{S}$ .

5

10

15

20

25

30

35

40

45

50

55